**Formation of $LiC_{10}$ and $LiC_8$ in chemically-lithiated single-walled carbon nanotubes**

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Graphite forms different phases with alkali-metals M depending on M and the synthesis conditions. Stage-1 intercalation compounds (with alternating graphene and metal layers) were reported for all alkali-metals, sodium being the exception. For heavier metals (K, Rb, Cs), normally the stable stage-1 compound containing the most metal has a $MC_8$ composition. With lithium the stable composition is $LiC_6$. The in-plane metal distribution is hexagonal in both the $MC_8$ and $LiC_6$ structures, although with different metal-metal spacings. To date, however, $LiC_8$ has not been observed.

In this work we show the formation of new Li-carbon phases in lithiated single-walled carbon nanotubes (SWNTs). As starting material, we used purified (SWNTs) prepared by pulsed laser vaporization and shaped as a matted thin film. The material was evacuated at 150°C overnight, then reacted with molten lithium at 220°C for two weeks. This resulted in a deep chemical lithiation as indicated by the gold color characteristic of stage-1 Li-intercalated graphite.

The crystal structure of chemically lithiated SWNTs was investigated by x-ray diffractometry (XRD), transmission electron microscopy (TEM), and electron diffraction. Raman spectroscopy was also used before and after lithiation.

The XRD pattern of Figure 1 is consistent with a monoclinic unit cell with an in-plane $\sqrt{7}x\sqrt{3}$ atomic arrangement corresponding to the composition $LiC_{10}$. The c-axis parameter was found close to 3.9 Å, 5% larger than in graphite $LiC_6$. The TEM observations showed a multi-phase system including the presence of $LiC_{10}$. The occurence of $LiC_8$ is shown clearly in Figure 2, where diffraction rings of polycrystalline graphite are observed together with a single crystal diffraction pattern of $LiC_8$ projected along the [001] zone axis. The 4.26Å d-spacing of the <100> spots are in agreement with calculations for the planar $LiC_8$ unit cell.

Evidently a significant fraction of the SWNT transforms to graphene-like strips in the presence of highly reactive molten lithium. Lithium is then intercalated between the C-nano-strips, taking the structure of $LiC_{10}$ as the major component and $LiC_8$.

Raman spectra showed a shift and/or splitting of the $A_{2g}$ radial (breathing) mode from 83 $cm^{-1}$ to a single 117 $cm^{-1}$ or to a triplet 114 $cm^{-1}$, 75 $cm^{-1}$ and 61 $cm^{-1}$ depending on the lithium content. The two $E_{2g}$ modes at 1562 $cm^{-1}$ and 1587 $cm^{-1}$ yielded a single mode at 1576-1578 $cm^{-1}$ after lithiation.

The electrochemical cycling of SWNTs showed a large initial irreversible capacity. The reversible capacity did not exceed 250 mAh/g.

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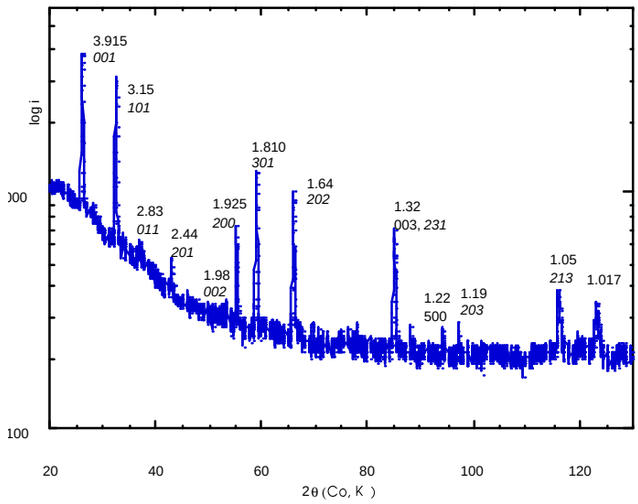
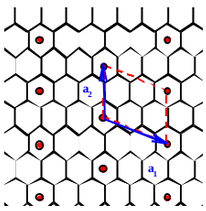



Figure-1: Top: XRD pattern of Li-SWNTs with line indexing in the $\sqrt{7}x\sqrt{3}$ Li-superlatice of $LiC_{10}$ (major phase, schematic in-plane structure see left).




100-graphite

100-$LiC_8$

Figure-2: Top: Electron diffraction pattern of lithiated SWNT showing the 2x2 Li-superstructure $LiC_8$ (minor phase, schematic in-plane structure see left).